

*Heats of Combustion and Formation of Nitro-Compounds.**Part I.—Benzene, Toluene, Phenol and Methylaniline Series.*

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Introduction.

The study of the explosive properties of organic nitro-bodies is not complete without a knowledge of their heats of formation, for these constants are closely related to their stability and sensitiveness to impact and heat. The heats of formation also form the basis of any calculations of the energy liberated in the detonation of high explosives. The heats of detonation of balanced explosives such as a mixture of ammonium nitrate and trinitrotoluene arranged for complete combustion, can readily be determined from the heats of formation. When there is insufficient oxygen in the explosive for the complete combustion of the hydrogen and carbon it is more difficult to calculate the heat of detonation, especially as the composition of the products is dependent on the external work done by the gases, but from a knowledge of the constants of gaseous and heterogeneous equilibria it is often possible to obtain values with some degree of accuracy. The preliminary work in the production of new explosives can often be considerably shortened by such calculations.

The heats of combustion of some of the members of the toluene, benzene and phenol series have been determined by various workers, but there are many gaps in the series, and the agreement in certain cases is unsatisfactory. These results are summarised in Table I.

In order to amplify these data, it was decided to carry out an accurate estimation of the heats of combustion and formation of the nitro-compounds in the toluene, benzene, phenol and methylaniline series, and to calculate both the heats due to the entrance of a nitro-group into members of the series and the heats of nitration.

The toluene series was investigated in greater detail, since all of the isomers in this series were available. The constants of only the principal members of the other series have been determined.

Apparatus and Methods of Manipulation.

The calorimetric system consisted of a Berthelot-Mahler-Kroeker bomb placed in a nickel-plated copper vessel containing 1200 c.c. of water; this vessel was surrounded by another larger similar vessel, the whole standing

Table I.—Heats of Combustion of Nitro-compounds as given by Previous Observers.

Series.	Substance.	Mol. wt.	Heat of combustion.			Heat of formation.	Observer.
			Grm. cal. per grm.	Kgrm. cal. per mol.			
				Const. vol.	Const. press.		
Toluene.....	<i>m</i> -Nitrotoluene	137	—	889·4	889·6	11·0	Swarts.
	Trinitrotoluene—						
	2 : 4 : 6.....	227	—	—	—	7·7	From Bichel's figures.
	2 : 4 : 6.....	227	—	—	—	5·9	Koehler.
	Crude T.N.T.	227	—	—	880·8	1·8	Will.
Benzene	Nitrobenzene	123	—	734·8	734·7	3·9	Swarts.
	<i>m</i> -Dinitrobenzene	168·05	—	695·3	695·1	8·6	Swarts.
	<i>o</i> -Dinitrobenzene.....	168·05	4194	704·8	703·7	—	B. Matignon.
	<i>m</i> -Dinitrobenzene	—	4155	698·3	697·3	—	B. Matignon.
	<i>p</i> -Dinitrobenzene	—	4146	696·7	695·6	—	B. Matignon.
	1 : 3 : 5-Trinitrobenzene	213·05	3126	666·1	664·0	—	B. Matignon.
Phenol	1 : 2 : 4-Trinitrobenzene	—	3195	680·8	678·6	—	B. Matignon.
	<i>o</i> -Nitrophenol	139·05	4954	688·8	688·4	—	Matignon, Deligny.
	<i>p</i> -Nitrophenol	—	4960	689·7	689·3	—	Matignon, Deligny.
	<i>o</i> -Nitrophenol	—	—	688·5	688·0	50·1	Swarts.
	<i>m</i> -Nitrophenol	—	—	684·8	688·4	53·7	Swarts.
	<i>p</i> -Nitrophenol	—	—	688·6	688·2	50·0	Swarts.
Aniline	Picric acid	229·05	—	—	618·4	50·9	Sarrau and Vielle.
	Picric acid	—	—	—	—	50·2	Koehler.
	<i>o</i> -Nitraniline	138	—	766·2	765·9	6·9	Swarts.
	<i>m</i> -Nitraniline	—	—	766·6	766·3	6·5	Swarts.
	<i>p</i> -Nitraniline	—	—	760·5	760·2	12·3	Swarts.
	Trinitraniline	228	—	—	—	15·2	Koehler.
	Tetryl	287	—	—	—	40·8	Koehler.

within a copper water jacket. A thick felt covering protected the whole system from outside influences, and closely fitting cardboard lids prevented air currents from entering. The air space in the inner calorimeter was reduced to a minimum to avoid convection currents, and the volume of water was as small as was consistent with good stirring.

The water equivalent was determined by means of the secondary standards, naphthalene and benzoic acid. There is, however, some confusion in the literature as to the best values for the mechanical equivalent of heat and the secondary standards. The three main secondary standards, naphthalene, benzoic acid and cane sugar, have in turn been criticised by different authors. Their usefulness appears to be in the order given. The values of the heats of combustion of these substances are still uncertain to the extent of two to three parts per thousand. This is due chiefly to the different values taken for the mechanical equivalent of heat by German and by American workers, but even the ratios of the heats of combustion of different substances obtained by different workers are unsatisfactory. The determinations of Roth, Fischer and Wrede, Wrede and the American Bureau of Standards are based on electrical methods which have been carried out with great care. These together with data from other authors are summarised below :—

Table II.—Heats of Combustion of Secondary Standards by various Observers.

No.	Substance.	Cal./gram.	Joules per gram.	Observer.
2	Naphthalene	9624 (Roth.)	40314	Wrede, 'Zt. Phys. Chem.,' vol. 75, p. 92 (1910).
1	"	—	40384	Fischer, 'Sitz. Akad. Wiss. Berlin,' vol. 15 (1904).
—	—	—	40350	Wrede, Swientoslawski, 'J. A. C. S.,' vol. 39, p. 2598 (1917).
5	"	9612	—	Dickinson, 'Bureau of Standards Sci. Paper,' 130.
6	"	9613	—	Swientoslawski, 'J. A. C. S.,' p. 2598 (1917). [(1915).
3	"	9636	—	Roth, 'Lieb. Ann.,' vol. 407, p. 127
4	"	9628	—	Stohmann, 'J. Prakt. Chem.,' (II), vol. 40, p. 77 (1889).
2	Benzoic acid	6318 (Roth.)	26466	Wrede.
1	" "	—	26475	Fischer, 'Zt. Phys. Chem.,' vol. 69, p. 234 (1909).
5	" "	6323	—	Dickinson.
6	" "	6311	—	Swientoslawski.
4	" "	6322	—	Stohmann.

The concordance between these heats of combustion is not altogether satisfactory, either with respect to agreement between absolute values or

between the ratios of the heats of combustion of the two substances as has been pointed out by Swientoslawski (*loc. cit.*).

The ratios for naphthalene and benzoic acid have been recalculated and are given in the following Table :—

Table III.—Ratio of Heats of Combustion of Naphthalene and of Benzoic Acid.

No.	Author.	$\frac{\text{Heat of combustion of naphthalene}}{\text{Heat of combustion of benzoic acid}}$	Date.
1	Fischer and Wrede	1·5254	1904
2	Wrede	1·5233	1910
3	Roth	1·5235	1915
4	Stohmann	1·5229	1889
5	Dickinson	1·5202	1915
6	Swientoslawski	1·5232	1917
7	Research Department, Woolwich	1·5240	1918

Of these values the highest (1) must be regarded as superseded by (2), and (5) ought to be eliminated on the showing of Swientoslawski. The mean of the four remaining values (1·5232) is the same as that determined by Swientoslawski, and it seems advisable to accept this value provisionally. The German author Roth (see Landolt and Börnstein's Tables) has assumed the mechanical equivalent of heat to be 4·189 ergs, the value of the Reichsanstalt, Berlin, while (5) and (6) in Table II are based on the figure 4·182 ergs, the value of Harvey and Davis, Harvard.

Since the determination by the American Bureau of Standards agrees with that of Swientoslawski and is more recent than that of Roth and Wrede, the 15° value of 9613 cal./gram. may be provisionally accepted for the heat of combustion of naphthalene, and from the above consideration of the ratios the most reliable value for benzoic acid is 6311 for the 15° calorie. To make the results in this paper directly comparable with those of Richards* the 18° calorie is taken in this work as the unit, making the heat of combustion of naphthalene 9622 cal./gram. and of benzoic acid 6317 cal./gram. These values are employed for the determination of the water equivalent of the system.

The mean value obtained by calibration with benzoic acid was 1544·8 cal./gram. The ratio of the heats of combustion of naphthalene

* 'J. A. C. S.,' vol. 39, p. 341 (1917). Since this paper was written Richards and Davis ('J. A. C. S.,' vol. 42, p. 1599 (1920)) have re-determined the heats of combustion as follows :—Benzoic acid, 6320 ; naphthalene, 9614 (18° calories per gram.). These results show that there is still uncertainty in the values of the secondary standards.

Table IV.—Water Equivalent of System, by Combustion of Naphthalene.

Substance.	No. of Beckmann thermometer.	Weight.	Temp. rise.	Water equivalent.
Sample 2— M.P. 80·3–80·5° C.	No. 2	gm. 0·4822	° C. 3·004	1544·4
	"	0·4989	3·108	1544·4
	1329 No. 14	0·3302	2·060	1542·4
	"	0·3201	1·994	1544·5
	"	0·3985*	2·499	1542·0
	P.T.R. 59334	0·3952*	2·4745	1544·3
	"	0·4055	2·525	1545·3

* In the two cases marked with an asterisk 0·0046 gm. cotton-wool (heat of combustion 4020 calories per gramme) was used to facilitate ignition of the pellet of naphthalene.

and benzoic acid was found to be 1·5240, which differs by 8 in 15,000 from the mean ratio in Table III.

Owing to the variations in the published heats of combustion of benzoic acid, and the difficulties which occur in its purification, the value obtained with naphthalene, 1544, is considered the more accurate, and so was adopted as the water equivalent of the system.

All the solid substances were burnt in the form of pellets, and were fired electrically by platinum wire of 0·004 inch diameter, and a battery of 12 volts. In order to avoid overheating of the top of the bomb and too rapid combustion of the substance, the weight taken was such as to give a rise in temperature of not more than 1·5° C. and 2° C. The bomb was twice filled with oxygen to a pressure of 5 atmospheres and emptied, before finally filling to a pressure of 20 atmospheres of oxygen. The percentage of atmospheric nitrogen was thus greatly reduced, so that the nitric acid which did form was mainly due to the nitrogen in the explosive. The rate of stirring was kept constant at about seventy strokes per minute.

In the case of liquids such as nitrobenzene, a modification of Richards' method* was used. At first, the nitrobenzene was placed in a thin glass bulb at the bottom of the crucible, and ignited with a tuft of cotton-wool and paraffin-wax, as in Richards' method. Residues of carbon were left on the top and the walls of the bomb, and, although there was no smell of nitrobenzene, the heats of combustion were irregular. Fairly satisfactory results were obtained if the unconfined liquid lay at the bottom of the crucible and Richards' method of ignition employed. With this method of firing, the nitrobenzene was completely consumed, and no smell of nitrobenzene was

* 'J. A. C. S.,' vol. 39, p. 341 (1917).

observed in the products of combustion. All the liquids investigated were fired by this method.

The corrections applied to obtain the heats of combustion at constant pressure were:—

- (i) Radiation correction.
- (ii) Correction for calibration of the thermometer.
- (iii) Correction for the heat of formation of the nitric acid produced.
- (iv) Correction of the gases to constant pressure.

(i) The maximum temperature being nearly reached at the end of the first minute, a short method was found to give the radiation correction sufficiently accurately.

(ii) The thermometer used was at first Beckmann No. 2, N.P.L. 13, and, later, Beckmann 1329, N.P.L. 14, both of which had been standardised to 0.002° C. The water equivalent was not appreciably altered by changing the thermometer.

(iii) The nitric acid produced during the combustion was estimated, and correction applied for the heat of formation of nitric acid.



The correction (due to nitric acid) is about 1 to 1.5 kgrm.-cal./mol. for mononitro-compounds, and increases to 1.7 to 2.6 for trinitro-compounds. The amount of nitric acid formed was somewhat variable, probably owing to irregularities in the rate of combustion of the nitro-compound. It was therefore necessary to determine and allow for the nitric acid produced in every experiment.

(iv) To convert the molecular heat of combustion at constant volume to the molecular heat of combustion at constant pressure, 0.54 + 0.0021 kgrm.-cal. is subtracted for every mol. of gas formed, and added for every mol. of oxygen used up in the combustion of one mol. of substance. It is assumed that the whole of the water formed becomes liquid, and the error thus introduced does not affect the fifth figure in the value of the heat of combustion.

The value 0.58 kgrm.-cal., corresponding to a temperature of 20° C., has been used.

Purification of Nitro-compounds.

The substances in the toluene and benzene series were supplied by the organic laboratory of the Research Department, and the solids had been purified until a constant melting point was obtained. The melting points and some boiling points are given in Table V.

Table V.
Melting Points of Nitro-compounds.

Substance.	Melting point.	Substance.	Melting point.
	° C.		° C.
Paranitrotoluene	52·1	<i>m</i> -Dinitrobenzene	90·0-90·1
2 : 3-Dinitrotoluene	59·6	Trinitrobenzene (Sym.)	122·1-122·4
2 : 4-Dinitrotoluene	70·5	<i>o</i> -Nitrophenol	45·1
2 : 5-Dinitrotoluene	51·2	<i>p</i> -Nitrophenol	113·1-113·9
2 : 6-Dinitrotoluene	64·3	2 : 4-Dinitrophenol	111·2-111·8
3 : 4-Dinitrotoluene	58·9	Picric acid	120·6-121·1
3 : 5-Dinitrotoluene	92·8	Paranitromethylaniline	151·6-151·9
α -Trinitrotoluene	81·1	Dinitromethylaniline	177·6-177·9
β -Trinitrotoluene	110·9-111·0	Trinitromethylaniline	110·4-110·8
γ -Trinitrotoluene	102·7-103·3	Tetryl	128·7-129·1
δ -Trinitrotoluene	132·0-132·3	Methyl tetryl	99·9-101·1
ϵ -Trinitrotoluene	95·8		
ζ -Trinitrotoluene	110·0		

Boiling Points of Nitro-compounds.

Substance.	Boiling point.
<i>o</i> -Nitrotoluene	222·3-222·7 (772 mm.)
<i>m</i> -Nitrotoluene	234·0-235·4 (772 mm.)
Nitrobenzene	211·1-211·3 (771 mm.)
Monomethylaniline	195·1-195·6

Heat of Combustion.

The collected results of this investigation are given in Tables VI to XIII. The values for benzene and toluene are Richards'* and are based on the 18° calorie, and calculated on the weight of substances *in vacuo*. The value for phenol is Berthelot's.† All other values were obtained by experiment in the same calorimetric system and calculated on the weight of substance in air. The heats of combustion of isomeric forms are found to differ considerably, the differences being altogether outside the limits of error for any one isomer.

An analysis of the results for each substance shows some small divergence for any given substance, and the variation was not diminished by an improvement in the calorimetric system. The explanation of this probably lies in the great rapidity with which nitro-compounds burn in oxygen. For example, it was found dangerous to burn more than 0·5 grm. of tetryl in the bomb, as spitting caused injury to the porcelain lining. A greater divergence may be expected among the more highly nitrated bodies, and this is borne out by an analysis of the Table.

* 'J. A. C. S.,' vol. 37, p. 1919 (1915).

† 'Ann. Chim. Phys.,' 6, vol. 10, p. 433 (1887).

No member of the methylaniline series, except tetryl, has given trouble in this respect, and the widest variation amongst the results for this series amounts to about 6 in 4500.

Heat of Formation.

The values for the heats of formation are calculated from the heats of combustion at constant pressure, both on the diamond and on the amorphous carbon basis, using the heats of formation given below.

Substance.	Heat of formation.	Observer.
Water	68.3 kgrm.-cal./mol.	Thomsen.
Carbon dioxide	97.0 kgrm.-cal./mol. (C. amorphous)	Thomsen.
	94.3 kgrm.-cal./mol. (C. diamond).....	Berthelot.

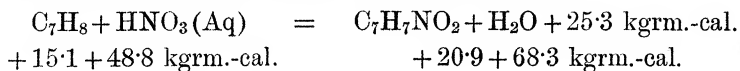
The heats of formation of the nitro-compounds from amorphous carbon have been employed in calculations of the heats of detonation of high explosives, more especially as the deposited carbon from many high explosives deficient in oxygen is in the amorphous form. The heats of formation given in Tables VII, IX, XI, and XIII refer to that phase of the substances which exists at 15° C. In fig. 1 the heats of formation (amorphous carbon) are plotted against the number of nitro-groups in the molecule. The heats of formation in these cases are corrected to the solid state from values of the heats of crystallisation given in the Tables.

Heat of Entry of Nitro-group.

The heat of entry of the nitro-group into the molecule is given by the difference between the heats of formation of the substance and that of the next higher stage of nitration, and values obtained in this way for toluene are to be found in Table XIV.

Heat of Nitration.

The heats of nitration (Tables VII, IX, XI, and XIII) are calculated from the heats of formation in accordance with the equation:—



The values thus represent the heat which would be evolved in the nitration of the substances with aqueous nitric acid.

Fig. 2 shows the effect of the number of nitro-groups in the molecule on the heat of nitration for each stage, all substances being in the solid form. In the case of the toluenes, fig. 3 gives the heats of nitration in another form, which illustrates the effects of nitration in the ortho-, meta-, and para-positions to existing nitro-groups.

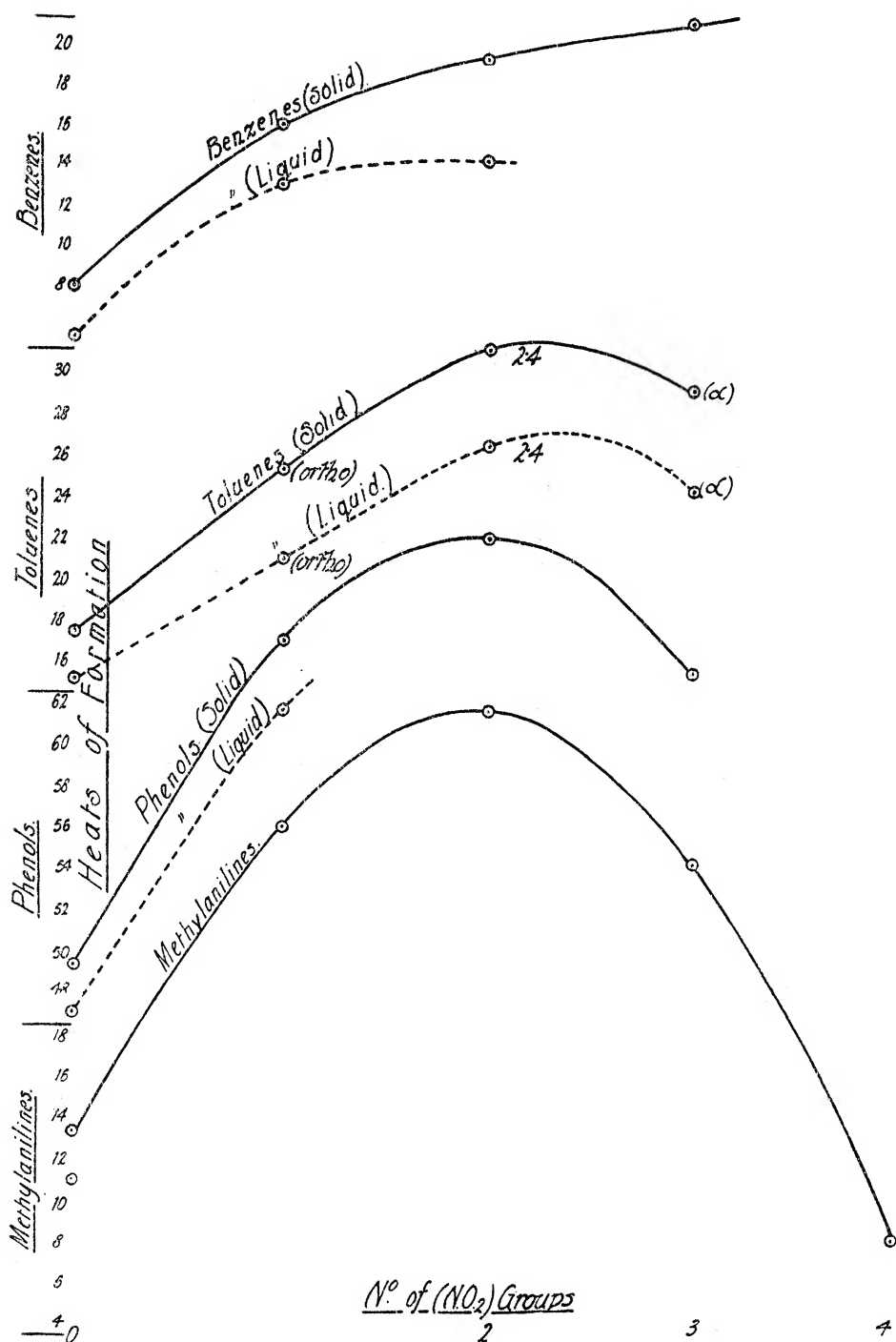


FIG. 1.

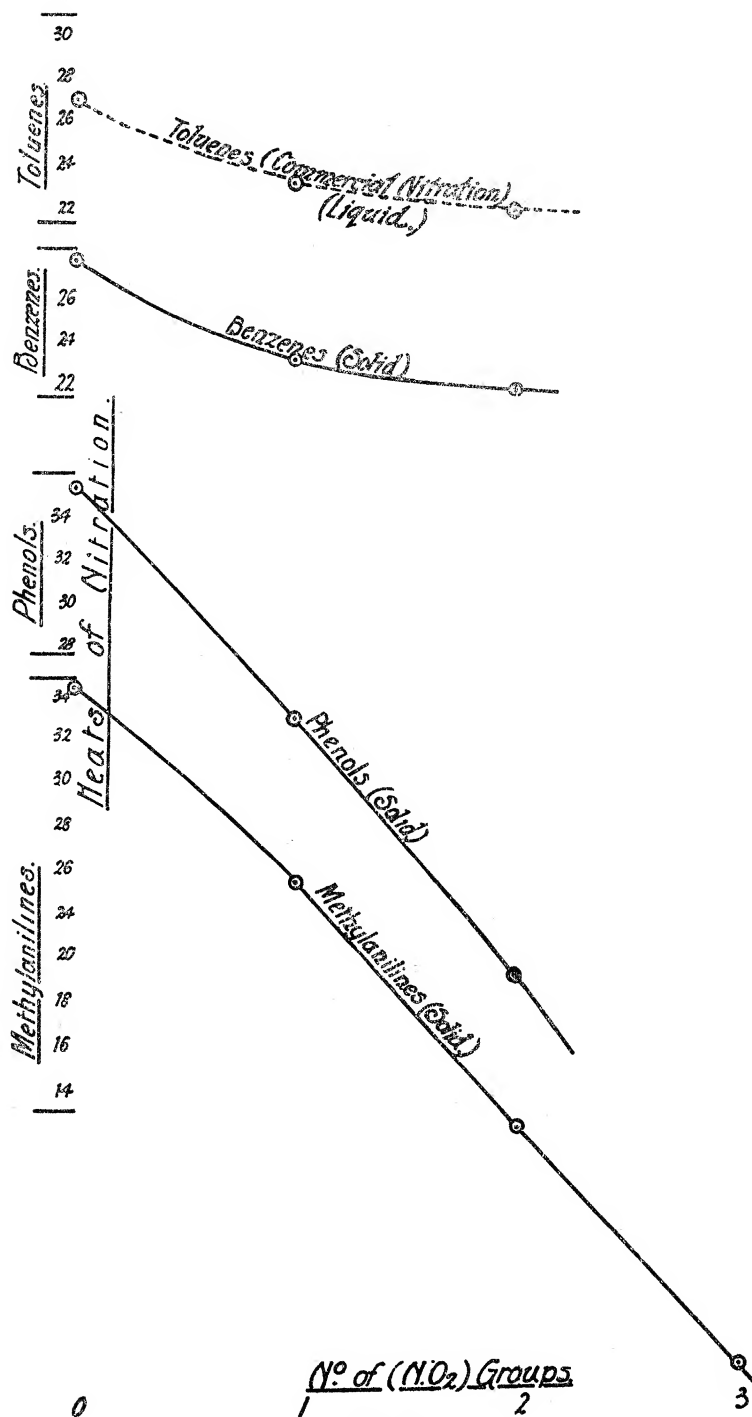


FIG. 2.

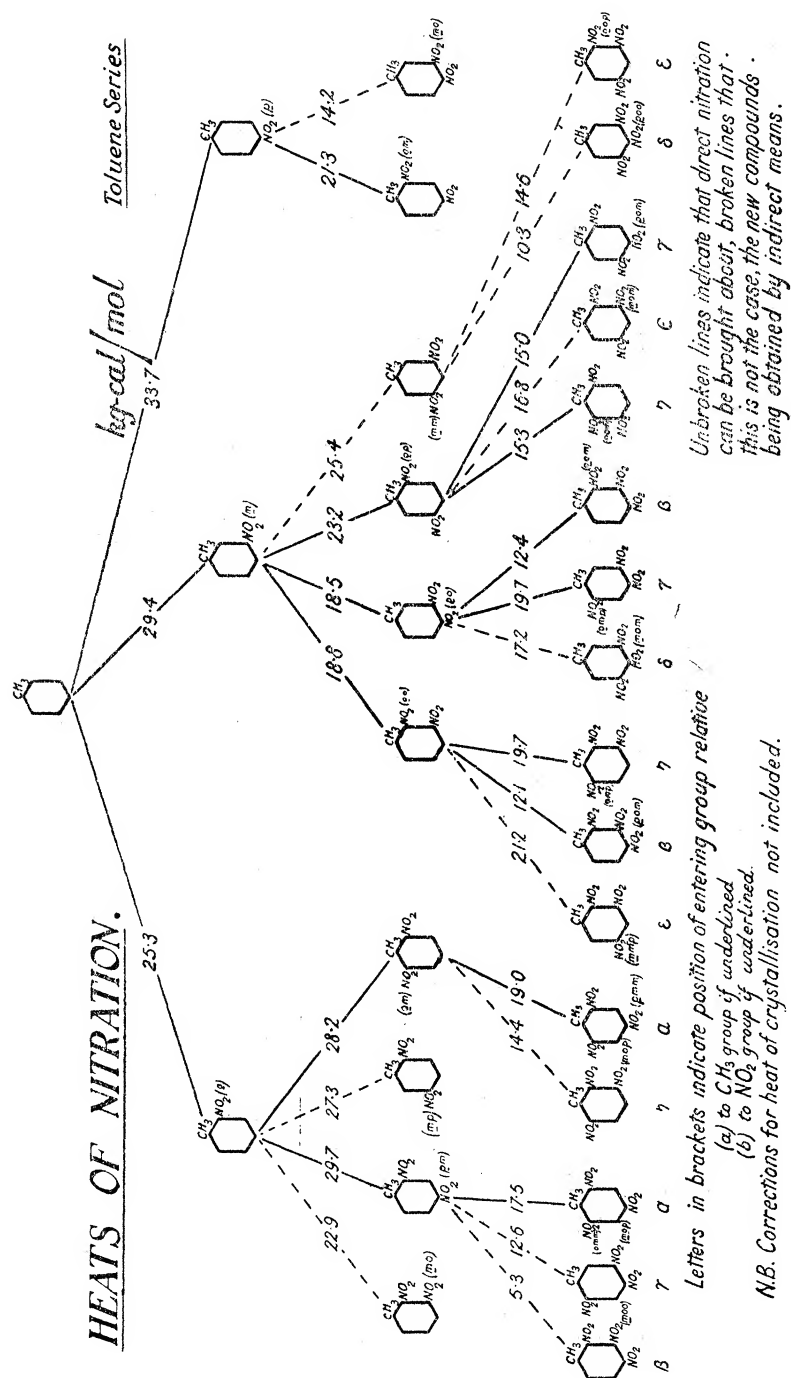


Fig. 3.

Heat of Crystallisation.

Some of the heats of crystallisation of members of the benzene, toluene and phenol series are known, and these are included in the following tables; but no data are available as to heats of crystallisation of isomeric nitro-bodies.

In order to determine to what extent the differences in the heats of formation of the isomeric trinitrotoluenes are affected by differences in the heats of crystallisation, the heats for the trinitrotoluenes were compared with Tammann's* value (4.88) for α -trinitrotoluene by a method involving measurement of rate of cooling.

The heats of crystallisation of β - and γ -T.N.T. were found to be 5.0 and 5.4 cal./mol. respectively; it is therefore considered that the large differences observed in the heats of combustion of the isomeric nitrotoluenes cannot be accounted for by differences in the heats of crystallisation.

Results.

(a) *Toluene Series.*—The nitrotoluenes form a complete series of isomeric bodies and are very suitable for an investigation into the relationship between the internal energy of isomeric bodies and their chemical constitution. The heats of combustion of the isomers of mono-, di- and tri-nitrotoluenes given in Table VI indicate that the internal energies of the various isomers vary considerably; thus the total variation in the dinitrotoluenes is 7.1 kgrm. cal./mol. and for trinitrotoluenes 12.2 kgrm.-cal./mol. The heats of combustion of the trinitrotoluenes run generally in line with their figures of insensitiveness and stability (Table VII) so that the isomer with the greatest internal energy (strain) is the most sensitive. Thus, β -trinitrotoluene is more sensitive than α -trinitrotoluene, and its heat of combustion is found to be higher.

Table VI.—Heats of Combustion of Toluene Series.

Substance.	Mol. wt.	Cal./grm. in oxygen uncorrected for nitric acid. (Average.)	Kgrm.-cal./mol. in oxygen uncorrected for nitric acid. (Average.)	Kgrm.-cal./mol. at constant volume corrected for nitric acid.
Toluene	92	—	—	935.9 (Richard's value).
Mononitrotoluene	137			
Ortho (liquid)	—	6569 } 6550 } 6548 } 6559 *6567 }	900.0 } 897.4 } 897.1 } 898.2 *899.7 }	897.0
Meta (liquid)	—	6528 } 6520 } 6527 6333 }	894.4 } 893.2 } 894.2 895.1 }	892.9

* Tammann, 'Zeit. Phys. Chem.,' vol. 85, p. 283 (1913).

Table VI.—continued.

Substance.	Mol. wt.	Cal./gram. in oxygen uncorrected for nitric acid. (Average.)	Kgram.-cal./mol. in oxygen uncorrected for nitric acid. (Average.)	Kgram.-cal./mol. at constant volume corrected for nitric acid.
Mononitrotoluene (<i>cont.</i>)				
Para	—	6490 } 6490 } 6496 } 6501 }	889.1 } 889.1 } 889.9 } 890.6 }	888.6
		6494	889.7	
Dinitrotoluene	182			
2 : 3	—	4743 } 4734 } 4730 }	863.2 } 861.6 } 860.0 }	860.5
		4736	861.9	
2 : 4 (two samples).....	—	4711 } 4697 } 4700 }	857.4 } 854.8 } 855.4 }	853.7
		4700	855.4	
2 : 5	—	4701 } 4693 } 4711 }	855.5 } 854.0 } 857.3 }	856.1
		4713	857.7	
2 : 6 (two samples)	—	4718 } 4717 } 4715 }	858.6 } 858.4 } 858.2 }	855.2
		4710	857.7	
3 : 4 (two samples)	—	4705 } 4701 } 4736 }	856.4 } 855.6 } 861.9 }	860.8
		4739	862.4	
3 : 5	—	4741 } 4741 } 4699 }	862.9 } 862.8 } 855.2 }	853.9
		4699	855.2	
Trinitrotoluene	227			
α (2 : 4 : 6)	—	3631 } 3622 } 3629 }	824.2 } 822.2 } 823.7 }	822.5
		3630	823.9	
β (2 : 3 : 4).....	—	3638 } 3628 } 3687 }	825.8 } 823.6 } 837.2 }	834.7
		3684	836.3	
γ (3 : 4 : 6).....	—	3679 } 3689 } 3652 }	835.2 } 836.4 } 828.9 }	827.4
		3654	829.4	
δ (3 : 4 : 5)	—	3654 } 3667 } 3667 }	829.6 } 829.6 } 832.4 }	829.9
		3667	832.3	
ϵ (2 : 3 : 5)	—	3666 } 3643 } 3645 }	832.1 } 826.9 } 827.4 }	825.6
		3648	828.0	
ζ (2 : 3 : 6)	—	3655 } 3647 } 3647 }	829.6 } 828.0 } 828.0 }	827.1
		3647	827.0	
		3643 } 3645 } 3653 }	827.0 } 827.4 } 829.2 }	
		3647	828.0	

* Air not driven out of bomb. Correction made independently.

Table VII.—Summary of Heats of Combustion, Formation and Nitration per Molecule, and Figures of Insensitiveness.

Substance.	Mol. wt.	Heat of combustion (kgm.- cal./mol.).		Heat of formation (kgm.-cal./mol.).		Heat of nitration (kgm.-cal./mol.).				Heat of crystallisa- tion (kgm.- cal./mol.).	Gas evolution at 120° C. in c.c. per 40 hours.	Figure of insensitive- ness (picric acid = 100.).
		Const. vol.	Const. press.	C. amorph.	C. diamond.	One NO ₂ group inserted in the following positions relative to existing NO ₂ groups.						
						<i>o</i> -position.	<i>m</i> -position.	<i>p</i> -position.				
Toluene.....	92	935.9	937.1	+ 15.1	— 3.8	+ 25.3	+ 29.4	+ 33.7	2.4			
Mononitrotoluene— Ortho (liquid) ...	137	897.0	897.2	+ 20.9	+ 2.0	2:3+22.9	2:4+29.7 2:6+28.2	2:5+27.3				
Meta (liquid) ...	—	892.9	893.1	+ 25.0	+ 6.1	2:3+18.8 3:4+18.5	3:5+25.4	2:5+23.2	4.3			
Para	—	888.6	888.8	+ 29.3	+ 10.4	3:4+14.2	2:4+21.3	—				
Dinitrotoluene— 2:3	182	860.5	859.6	+ 24.3	+ 5.4	2:3:4+12.1	2:3:5+21.2	2:3:6+19.7 2:3:5+21.2 3:4:6 12.6				
2:4	—	853.7	852.8	+ 31.1	+ 12.2	3:4:6 12.6	2:4:6 17.5		4.80			
2:5	—	856.1	855.2	+ 28.7	+ 9.8	2:3:4 5.3 2:3:5 16.8 3:4:6 15.0	2:3:5 16.8 3:4:6 15.0					
2:6	—	855.2	854.3	+ 29.6	+ 10.7	2:3:6 15.3	2:3:6 15.3	2:3:6 14.4 3:4:6 19.7				
3:4	—	860.8	859.9	+ 24.0	+ 5.1	2:3:6 14.4 2:3:4 12.4	2:4:6 19.0 3:4:6 19.7					
3:5	—	853.9	853.0	+ 30.9	+ 12.0	3:4:5 17.2 2:3:5 14.6 3:4:5 10.3	—	2:3:5 14.6				
Trinitrotoluene— α (2:4:6)	227	822.5	820.7	+ 29.1	+ 10.2	—	—	—	4.88	0.08	114	
β (2:3:4)	—	834.7	832.9	+ 16.9	— 2.0	—	—	—	—	0.73	92	
γ (3:4:6)	—	827.4	825.6	+ 24.2	+ 5.3	—	—	—	—	1.40	102	
δ (3:4:5)	—	829.9	828.1	+ 21.7	+ 2.8	—	—	—	—	1.60	95	
ε (2:3:5)	—	825.6	823.8	+ 26.0	+ 7.1	—	—	—	—	0.40	101	
ζ (2:3:6)	—	827.1	825.3	+ 24.5	+ 5.6	—	—	—	—	—	—	

The heats of formation (carbon amorphous) (Table VII) of this series, range from 15 to 31 kgrm.-cal./mol. and in general rise to a maximum for the third (dinitro) member of the series. This maximum in the heats of formation is shown by fig. 1. Thus the course of the nitration of α -trinitrotoluene is traced from toluene, through orthonitrotoluene and 2:4 and 2:6-dinitrotoluenes. The heats of formation of the liquid substances as set forth in this curve are corrected to the solid form. Toluene is assumed to have heat of crystallisation 2.4 cal./mol. and the mononitrotoluenes 4.3 cal./mol.

Some regularities have been observed in the heats of formation of members of the toluene series. Thus there appears to be a definite increase in the internal energy (lower value for heat of formation) associated with groups in the ortho position, and especially when the nitro-groups are ortho to one another. A phenomenon which may be associated with this has been observed by Le Bas* who found in the case of the mononitrotoluenes that the greatest decrease in molecular volume was with ortho-substitution. For the present data for heat of formation the following expression approximately holds:—

Heat of formation of di- and tri-nitrotoluenes = $30.8 - 1.3(n \times 4m\epsilon)$ where n is the number of nitro-groups ortho to a methyl-group, and m is the number of nitro-groups ortho to a nitro-group.

The extent to which this obtains is shown in the following Table:—

Table VIIA.

Substance. (solid).	Heat of formation.		Substance (solid).	Heat of formation.	
	Calculated.	Experimental.		Calculated.	Experimental.
DNT—			TNT—		
2 : 4	29.5	31.1	α	28.2	29.1
2 : 3	24.3	24.3	β	19.1	16.9
2 : 5	29.5	28.7	γ	24.3	24.2
2 : 6	28.2	29.6	δ	20.4	21.7
3 : 4	25.6	24.0	ϵ	24.3	26.0
3 : 5	30.8	30.9	ζ	23.0	24.5

Heats of nitration of the toluene series are calculated from heats of formation and are tabulated in Table VII. The heats of nitration of the liquid isomers are uncorrected for change of state, and the amounts of the heat evolved at each stage of the nitration from toluene to the trinitro-compounds are given for all possible entries of the NO_2 group into the ring. The heat of nitration ranges from +33.7 kgrm.-cal./mol. for toluene to p -nitrotoluene to 5.3 kgrm.-cal./mol. for 2:4 dinitrotoluene to β -trinitrotoluene.

* 'The Molecular Volumes of Liquid Compounds,' p. 220.

This Table is made clearer by reference to fig. 3. The formulæ of the isomers are given and the methods of derivation of the substances are indicated. The numbers show the amount of heat liberated during the nitration when one NO₂ group is introduced in the ortho-, meta and para-positions to existing nitro-groups. The insertion of a nitro-group into the *o*-, *m*- and *p*-positions relative to existing nitro-groups, and to the methyl group is indicated in the diagram.

(b) *Benzene Series*.—The results are 4–5 kgrm.-cal./mol. higher than those of Swarts but agree with those of Berthelot (Table I).

Table VIII.—Heats of Combustion—Benzene Series.

Substance.	Mol. wt.	Cal./grm. in oxygen uncorrected for nitric acid.	Kgrm.-cal./mol. in oxygen uncorrected for nitric acid.	Kgrm.-cal./mol. corrected for nitric acid.
Benzene	78	—	—	780·4 (Richard's value).
Nitrobenzene	123	6022 } 6036 } 6020 } 6025 6028 } 6018 }	741·1	739·9
<i>o</i> -Dinitrobenzene	168	4195 } 4191 } 4198 4207 }	705·2	703·8
<i>m</i> -Dinitrobenzene	—	4181 } 4186 } 4180 4173 }	702·3	700·6
<i>p</i> -Dinitrobenzene	—	4140 } 4130 } 4138 4144 } 4137 }	695·2	693·7
1 : 3 : 5 Trinitrobenzene	213	3126 } 3133 } 3133 3140 }	667·3	665·6
1 : 2 : 4 Trinitrobenzene	—	3177 } 3172 } 3177 3186 } 3174 }	676·9	675·9

The heats of formation (Table IX) are lower than for the toluenes and do not give a maximum such as that obtained for the nitrotoluenes; the values rise from +5·6 for benzene to +26·1 for *p*-dinitrobenzene. The nature of the rise to the symmetrical trinitrobenzene is shown in fig. 1. Of the two isomeric trinitrobenzenes the symmetrical has the greater heat of formation and also possesses greater stability and has a higher figure of insensitiveness than the unsymmetrical compound (see below). This agrees with the behaviour of the trinitrotoluenes.

Table VIIIA.

Explosive.	Heat of formation (kgm.-cal./mol.).	Figure of insensitive- ness (picric acid = 100).	Gas evolution (c.c. in 40 hours) at 120° C.
1 : 3 : 5 trinitrobenzene.....	21.1	106	Nil
1 : 2 : 4 trinitrobenzene.....	10.8	103	0.66

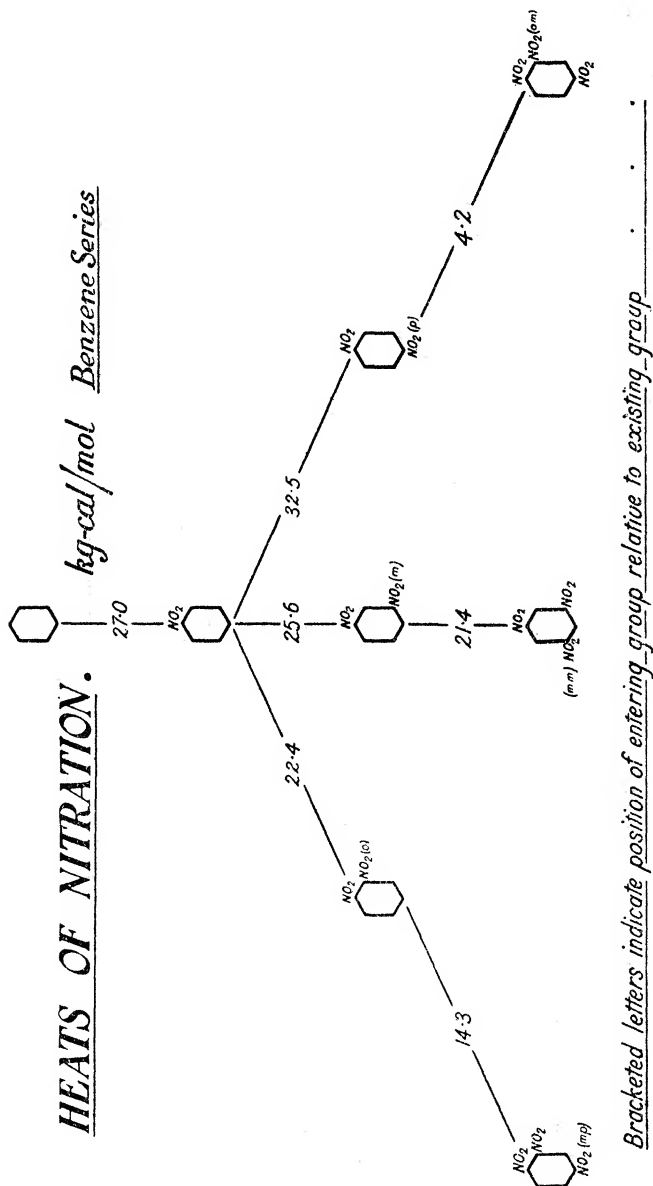


Fig. 4.

Table IX.—Heats of Combustion, Formation, Nitration and Crystallisation—Benzene Series.

Substance.	Mol. wt.	Heat of combustion, kgm.-cal./mol.		Heat of formation, kgm.-cal./mol.		Heat of nitration, kgm.-cal./mol.	Heat of crystallisation, kgm.-cal./mol.
		Const. vol.	Const. press.	C. amorph.	C. diamond.		
Benzene	78	780.4	781.3	+ 5.6	- 10.6	+ 27.0	2.35
Nitrobenzene	123	739.9	739.7	+ 13.1	- 3.1	+ 25.6	2.78
<i>o</i> -Dinitrobenzene	168	703.8	702.6	+ 16.0	- 0.2		
<i>m</i> -Dinitrobenzene	168	700.6	699.4	+ 19.2	+ 3.0	+ 21.4	4.87
<i>p</i> -Dinitrobenzene	168	693.7	692.5	+ 26.1	+ 9.9		
1 : 3 : 5-Trinitrobenzene	213	665.6	663.4	+ 21.1	+ 4.9		
1 : 2 : 4-Trinitrobenzene	213	675.9	673.7	+ 10.8	- 5.4		

Table XI.—Heats of Combustion, Formation, Nitration and Crystallisation—Phenol Series.

Substance.	Mol. wt.	Heat of combustion, kgm.-cal./mol.		Heat of formation, kgm.-cal./mol.		Heat of nitration, kgm.-cal./mol.	Heat of crystallisation, kgm.-cal./mol.
		Const. vol.	Const. press.	C. amorph.	C. diamond.		
Phenol	94	736.9	737.5	+ 49.4	+ 33.2	+ 35.0	2.34
<i>o</i> -Nitrophenol	139	689.9	689.4	+ 63.4	+ 47.3	+ 24.5	4.30
<i>p</i> -Nitrophenol	139	687.0	686.5	+ 66.3	+ 50.1	+ 12.9	
2 : 4-Dinitrophenol	184	650.2	648.7	+ 69.9	+ 53.7		
Picric acid	229	623.7	621.2	+ 63.3	+ 47.1		

The curve of heats of nitration is not so steep as for the phenol and methylaniline series, and this appears to be connected with the difficulty with which the nitro-group enters the molecule. The slope corresponding to the conversion of dinitrobenzene into trinitrobenzene is very slight, and it is well known that this step in the nitration proceeds only with great difficulty.

The variations in the heats of nitration of the isomers in the benzene series is indicated in fig. 4, where the same method is adopted as in fig. 3. The relative order of the heats of nitration into the ortho-, meta- and para-positions is similar to that found for the toluene series, ortho-substitution taking place with evolution of the least amount, and the para-substitution with the greatest amount of heat.

(c) *Phenol Series*.—The heats of combustion of the phenols are very low, owing to the presence of a hydroxyl group. The values for *o*- and *p*-nitrophenol are of the same order as those given in Table I. It should be noted, however, that the *o*-nitro-compound has the higher heat of combustion.

Table X.—Heats of Combustion—Phenol Series.

Substance.	Mol. wt.	Cal./gram. in oxygen.	Kgrm.-cal./mol. uncorrected.	Kgrm.-cal./mol. corrected.
Phenol	94	—	—	736·9 (Berthelot's value).
<i>o</i> -Nitrophenol	139	4962 4972 4981	691·1	689·9
<i>p</i> -Nitrophenol	139	4950 4950 4953		
		4972 4951	688·2	687·0
2 : 4 Dinitrophenol	184	3540 3546	651·9	650·2
		3543		
Picric acid.....	229	2723 2727 2743	625·4	623·7
		2731		

(d) *Methylaniline Series*.—The heats of formation rise to a maximum for the third member, dinitromethylaniline, and then rapidly decrease, until, for tetryl, a heat of formation + 7·5 is obtained.

Table XII.—Heats of Combustion—Methylaniline Series.

Substance.	Mol. wt.	Cal./grm. in oxygen.	Kgrm.-cal./mol. uncorrected for nitric acid.	Kgrm.-cal./mol. corrected for nitric acid.
Methylaniline	107	9127 } 9114 } 9119 9116 }	975.7	974.4
<i>p</i> -Nitromethylaniline	152	6090 } 6093 } 6090 6088 }	925.8	924.3
2 : 4-Dinitromethylaniline	197	4504 } 4510 } 4507 4506 }	887.9	885.5
2 : 4 : 6-Trinitromethylaniline	242	3562 } 3563 } 3564 3566 }	862.5	859.9
Tetryl	287	2950 } 2951 } 2955 2955 } 2957 } 2964 }	848.1	845.3
Methyl Tetryl	301	3375 } 3366 } 3371	1014.7	1012.1

Table XIII.—Heats of Combustion, Formation and Nitration—Methylaniline Series.

Substance.	Mol. wt.	Heat of combustion, kgrm.-cal./mol.		Heat of formation, kgrm.-cal./mol.		Heat of nitration, kgrm.-cal./mol.
		Const. vol.	Const. press.	C. amorph.	C. diamond.	
Methylaniline	107	974.4	975.4	+ 11.0	— 7.9	+ 36.4
<i>p</i> -Nitromethylaniline ...	152	924.3	924.3	+ 27.9	+ 9.0	+ 25.2
2 : 4-Dinitromethylaniline	197	885.5	884.5	+ 33.5	+ 14.7	+ 11.9
2 : 4 : 6-Trinitromethylaniline	242	859.9	857.9	+ 26.0	+ 7.1	+ 1.0
Tetryl	287	854.3	842.3	+ 7.5	— 11.4	
Methyl tetryl	301	1012.1	1009.3	+ 5.8	— 15.8	

Table XIV.—Heat of Entry of Nitro-Group (into Solid Substances).

Substance.	<i>o</i> -position.	<i>m</i> -position.	<i>p</i> -position.
Toluene	+ 7·7	+ 11·8	+ 11·8
Nitrotoluene—			
2 (ortho)	2:3-0·9	2:4+5·9 2:6+4·4	2:5+3·5
3 (meta)	2:3-5·0 3:4-5·3	3:5+1·6	2:5-0·6
4 (para)	3:4-5·3	2:4+1·8	
Dinitrotoluene—			
2:3	2:3:4- 7·4	2:3:5+1·7	2:3:5+1·7 2:3:6+0·2
2:4	3:4:6- 6·9 2:3:4-14·2	2:4:6-2·0	3:4:6-6·9
2:5	2:3:5- 2·7 3:4:6- 4·5	2:3:5-2·7 3:4:6-4·5	
2:6	2:3:6- 4·2 2:3:6- 5·1	2:3:6-4·2 2:4:6-0·5	2:3:6-5·1
3:4	2:3:4- 7·1 3:4:5- 2·3	3:4:6+0·2	3:4:6+0·2
3:5	2:3:5- 4·9 3:4:5- 9·2	—	2:3:5-4·9

Conclusions.

The heats of formation of the nitro-compounds of the series investigated are markedly influenced by the position of the nitro-groups, and there is no regular change in these values similar to that observed in the introduction of the CH₂ group into aliphatic compounds; no empirical equation can be devised showing the relationships between the heats of formation of all aromatic nitro-compounds. From an examination of figs. 1 and 2, however, it is seen that certain regularities exist between the heats of formation and nitration of the benzene, toluene, phenol and methylaniline series. The heats of combustion in all of the series investigated decrease with increase in the number of nitro-groups, but the heats of formation tend to a maximum for the second or third member of the series, and then diminish. An exception is seen in the benzene series, but here it is probable that the maximum is shifted to the fourth member of the series, and that the same general relationship would hold if the more highly nitrated benzenes could be obtained.

It has been found in the toluene series that there is some regularity in the heats of formation of the di- and tri-nitroderivatives, and an expression is given on p. 227 which takes into account the lowering of this constant by nitro-groups, ortho to methyl, and to one another.

The introduction of the methyl group into benzene, to form toluene,

modifies only slightly the shape of the curves showing the heat of formation of the nitro-compounds, but the introduction of a hydroxyl- or methylamino-group has a marked effect. The resemblance between the curves for the phenol and methylaniline series is striking; the effect of the hydroxyl-group on the energy changes involved in nitration is thus very similar to that of the methylamino group, a result scarcely to be expected. The heats of nitration curves for these substances are straight lines. On the other hand, there is no simple additive relation for the entry of nitro-groups into the benzene and toluene series. The differences between the benzenes and toluenes on the one hand, and the phenols and methylanilines on the other, is apparently connected with the relative ease of nitration of these substances; the nitration of the former, especially to the highly nitrated members, takes place with difficulty, whereas the latter are easily nitrated.

In this connection also it may be mentioned that it is possible to nitrate phenol to the tetranitro-derivative, and methylaniline to the tetranitro-phenylmethylnitramine and pentanitrophenylmethylnitramine, while only the trinitro-derivatives of benzene and toluene have been obtained.

From the results of this study of the nitro-compounds of the benzene, toluene and phenol series, it is clear that the nearer the nitro-groups are to one another in the benzene ring the greater is the strain in the molecule and the lower the heat of formation. Thus the *o*-mononitro-compounds of these series have the smallest heat of formation; the differences between the ortho- and para- derivatives are, however, greatest for benzene and least for the phenol series. In the case of di- and tri- nitro-derivatives also, the proximity of the groups has the same effect.

The sensitiveness of nitro-compounds to impact and their comparative instability run in line with their heats of formation; thus β -trinitrotoluene, which has the lowest heat of formation, is the most sensitive to impact. The stability of the unsymmetrical trinitrotoluenes and benzenes is less than that of the symmetrical forms.

Certain conclusions can now be made with regard to the part played by the heat of formation in determining the magnitude of the heat of detonation of a high explosive. The large heat of formation of the nitro-phenols is a disadvantage from the point of view of their employment as explosives, though this is to some extent balanced by their comparatively high oxygen-content. Thus, although trinitrotoluene contains 29 per cent. less of the oxygen necessary for complete combustion than does picric acid, yet its heat of detonation is similar, namely 924 cal. per gramme (water gaseous), compared with 914 cal.* per gramme (water gaseous). This is to be expected

* Robertson, 'Trans. Chem. Soc.,' vol. 119, p. 8 (1921).

from the lower heat of formation of the trinitrotoluene (128 calories as compared with 277 calories per gramme for picric acid). In this example the introduction of the hydroxyl group into benzene to form phenol is accompanied by the absorption of more energy than that of the methyl group to form toluene, and this is reflected in the explosive phenomena.

From the figures that are available, the fifth member of a series, *i.e.*, a tetranitro-compound, will be seen to have a very low heat of formation. The effectiveness of tetryl as an explosive is very largely dependent on its being the fifth member of the methylaniline series and thus possessing a low heat of formation. The entry of the fourth nitro-group into the side-chain does not affect this uniformity.

Of the isomeric trinitrotoluenes, β -trinitrotoluene has been shown to have the lowest heat of formation, *i.e.*, to contain the lowest internal energy per gramme, and α -trinitrotoluene the highest heat of formation, *i.e.*, to contain the least internal energy per gramme. If on detonation these two substances gave the same products of decomposition, β -trinitrotoluene would have an advantage over α -trinitrotoluene of 54 cal. per gramme. For the same reason, the unsymmetrical trinitrobenzene should be a more powerful explosive than the symmetrical body. In general, the greater the number of adjacent groups in a molecule of a high explosive, the greater will be the heat of detonation, but there are often practical limitations to this choice on account of the greater reactivity and lower stability of the less symmetrical nitro-compounds.

We wish to tender our thanks to the Director of Artillery for permission to publish this work, and to Sir Robert Robertson for the interest he has taken in the investigation.
